

A STUDY OF THE INFLUENCE OF CAPILLARITY
ON THE MELTING POINT OF IODINE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
W. EVERETT LAND

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A STUDY OF THE INFLUENCE OF CAPILLARITY ON THE MELTING POINT OF IODINE¹

W. A. PATRICK AND W. E. LAND

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

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This study was undertaken with a view to accumulating additional evidence to support the capillary theory of adsorption (7). It was thought that support of the theory might be gained by the study of the adsorption of substances above and below the melting point. The reasoning was as follows: Above the melting point the adsorbed material would be in the liquid state and consequently the probability of its wetting the adsorbent would be greater than if it were in the solid state. If wetting occurred, then the curvature of the adsorbed material in the minute pits or capillaries of the adsorbent would be such as to produce a decrease of vapor pressure due to the tendency of the free surface energy to assume a minimum value. From this reasoning, it would be expected that the adsorption of vapors should increase at the solid-liquid transition point of the material adsorbed. In other words, the adsorption isotherm should exhibit a decided break in the curve at or above the melting point of the adsorbate.

The next question raised was that concerning the melting point of substances in small capillaries. Inasmuch as capillarity greatly influences the vapor pressure of highly curved surfaces, it follows immediately that the melting point must also be different in such a state than it is in bulk. These questions have been treated in detail in a later section of this paper. In this connection it is interesting to note that a recent paper by Kubelka (4) discusses this same subject. This article came to our attention after the completion of our experimental work.

Studies on solid adsorption (3) in which the adsorbent was kept well below the normal melting point of the substance adsorbed have been conducted in this laboratory. In the present work the adsorbent (silica gel) was kept below and above the normal melting point of the substance (iodine) adsorbed.

In order to facilitate the measurements a quartz fiber balance which has been described by McBain and Bakr (6) and by Cameron (1) was employed.

¹ From the dissertation submitted by W. E. Land to the Faculty of Philosophy of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

APPARATUS

The apparatus used in these measurements is represented diagrammatically in figure 1. The balance and gel were contained in a large glass tube, A, mounted in an air thermostat, T. A glass support, B, having sealed-in iron rods, on which the platinum bucket containing the gel rested, could be raised and lowered by means of a solenoid. This device was used so that the gel could be activated at rather high temperatures without affecting the balance. One hook of a small cylinder, C, supported the fiber balance, while the other was used for lowering in place with the aid of a thread or wire.

A second air thermostat, T', contained the substance to be adsorbed in a 50-cc. flask, D. The purpose of a similar flask, E, will be explained later. The glass tubing connecting tube A with flask D was wrapped with nichrome wire and heated electrically to prevent condensation of vapors. For

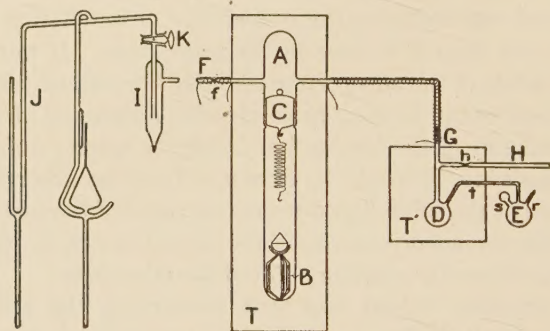


FIG. 1. APPARATUS USED

the same reason it was also heated from the thermostat, T, to constriction, f. This tubing contained an inner seal, G, which was broken at the proper time by a small pointed glass tube containing a sealed-in iron rod. The latter was raised to a suitable height by a magnet and allowed to fall on the seal. The side arms, F and H, were constricted so that they could be readily sealed from the pumps. Omission of stopcocks from the essential parts of the adsorption apparatus was necessary for two reasons: (1) continuous heating of glass; (2) action of vapors on grease. A trap, I, surrounded with a mixture of ether and dry ice, was inserted between the parts to be evacuated and the U-tube, J. This trap prevented the diffusion of foreign vapors and allowed the iodine to be distilled from the flask D to the trap I. In this manner the vapor of this substance could be swept through the apparatus.

The temperature of thermostats T and T' (figure 1) was automatically controlled within $\pm 0.2^\circ\text{C}$. by a mercury regulator and heating unit.

Thermometers used for both thermostats were calibrated. A motor-driven stirrer produced the necessary circulation.

The dimensions of the spring used in this work were as follows: average diameter of fiber, 0.010 in.; diameter of coils, 2 cm. The number of coils was twenty-seven. To relieve any strains, this spring, with an added load of about 0.5 g., was annealed for three days at 280°C.

The container for the adsorbent and also for the weights used in the calibration was made from platinum foil 0.0005 in. in thickness. This foil was made into a small bucket, the handle of which was No. 32 platinum wire. The finished bucket weighed $0.28 \pm g$.

Preliminary experiments were conducted to determine whether there was any reaction between the platinum foil and the substance (iodine) adsorbed. Under the experimental conditions no appreciable reaction was detected.

The balance was calibrated over a period of one month at temperatures which covered the experimental range, and the initial and final calibrations were within experimental error. Since the cathetometer used for measuring the extension of the balance could be read to within 0.03 mm., differences in weight of 0.1 mg. could be estimated.

A McLeod gauge, with which pressures of 10^{-6} mm. could be read, was used to determine the degree of evacuation before sealing. Two mercury diffusion pumps, connected in series, and an oil pump, with suitable traps, were used in all cases to obtain a high vacuum.

EXPERIMENTAL

Commercial silica gel, the particles of which were of uniform size, was selected and purified in the following manner. The gel was treated with concentrated nitric acid and heated, with constant stirring, to the boiling point. The nitric acid was poured off after the gel settled. This was repeated several times to remove large foreign particles. It was then refluxed with concentrated nitric acid for three days, washed with distilled water for several days, and dried in an oven at 110°C.

Mercury used for the McLeod gauge, etc., was carefully cleaned and distilled. Chemically pure iodine was further purified according to the method of Lundell, Hoffman, and Bright (5).

The purified gel, contained in an evaporating dish, was partially activated by placing it in a cylindrical furnace continuously heated to 320°C. A stream of nitrogen gas, dried with sulfuric acid and calcium chloride, was passed over the heated gel for two days. About 0.5 g. of this gel, weighed in the platinum bucket, was lowered on support B (figure 1) into a long glass tube, A, having two small side arms. The balance hanging on the support C was next lowered in place and the top of A closed. Connections with this tube were then made as shown in figure 1.

The system was evacuated to the inner seal, G, through side arm, F.

During this evacuation the gel was heated to about 350°C. by a small cylindrical furnace. Since it is very necessary to remove permanent gases, all glass tubing was continuously heated at temperatures higher than those at which adsorption isotherms were run. Evacuation and activation of gel usually required from three to five days. The McLeod gauge showed the pressure to be 5×10^{-6} mm. of mercury before constriction f was sealed.

In order to remove moisture before the introduction of iodine, the remainder of the system was baked and evacuated through the side arm H. This part of the system was then disconnected from the pumps by closing stopcock K. To exclude moisture, capillary r was broken through rubber tubing connected with two calcium chloride towers. A thin glass bulb on the side arm s was next broken and an excess of pure dry iodine quickly introduced into flask E. After having sealed both capillary r and side arm s, flask D was surrounded with dry ice. To remove permanent gases, the pumps were kept running while the iodine was being distilled. By gently heating E with an incandescent lamp, this distillation required about four hours. Flask E was then sealed off at constriction t, and the evacuation continued for several days. With the McLeod gauge showing about the same pressure as above, constriction h was sealed.

The bucket containing the gel was then hung on the balance and the weight of activated gel obtained from the extension it produced.

After the thermostat containing the gel was brought to the desired temperature and the iodine was surrounded with a mixture of ether and dry ice, the inner seal, G, was broken. There was no weighable adsorption at this temperature. The influence of the variation in the pressure of the iodine upon the amount of adsorption was studied by varying the temperature of the iodine. The iodine was first surrounded with a mixture of ice and water. Higher temperatures, chosen to give suitable points on the adsorption curves, were obtained by means of thermostat T'. In order to prevent ordinary distillation of the vapor, it is always necessary to keep the gel at a slightly higher temperature than the iodine.

Values given in the literature (2) enabled a vapor pressure-temperature curve to be plotted, from which the pressures of iodine at these temperatures were obtained.

Before each run the system was reëvacuated and the gel activated. This was accomplished by renewing the side arm F. It is not necessary to replace the broken inner seal, G, since the gel can be completely desorbed by surrounding the iodine with an ether-dry ice mixture. This arrangement also permitted iodine vapor to be swept through the system.

Adsorption isotherms were obtained at 70°, 92.5°, and 115°C. Immediately after the maximum adsorption was reached, for a particular run, the gel was desorbed by decreasing the temperature of the iodine. In each case, several values were obtained which agreed, within experimental error, with those for the adsorption process.

An isobar was obtained by keeping the temperature of the iodine constant and varying that of the gel. The vapor pressure of the iodine corresponding to this constant temperature was 17 mm.

The same sample of gel was used for these runs.

TABLE 1
Adsorption of iodine

p	x/m	p	x/m
mm. Hg		mm. Hg	
$T = 70^{\circ}\text{C}.$; weight of gel sample = 0.5700 g.		$T = 115^{\circ}\text{C}.$; weight of gel sample = 0.5700 g.	
0.03	0.0004	0.97	0.0014
0.471	0.0035	1.95	0.0030
1.03	0.0075	2.90	0.0039
1.50	0.0105	4.75	0.0060
2.16	0.0144	6.80	0.0077
2.95	0.0179	8.90	0.0102
4.31	0.0277	11.02	0.0126
Desorption		13.50	0.0158
2.16	0.0144	15.00	0.0170
1.03	0.0088	16.75	0.0189
0.03	0.0009	18.50	0.0210
		20.45	0.0236
		22.90	0.0268
		24.40	0.0280
		32.00	0.0360
		Desorption	
		20.45	0.0233
		15.00	0.0175
		8.90	0.0119
Run No. 2. $T = 92.5^{\circ}\text{C}.$; weight of gel sample = 0.5700 g.		Run No. 3. $T = 92.5^{\circ}\text{C}.$; weight of gel sample = 0.5700 g.	
1.03	0.0040	2.05	0.0072
2.05	0.0074	6.95	0.0202
2.90	0.0095	11.02	0.0316
4.60	0.0142	13.50	0.0385
6.95	0.0202	15.10	0.0453
9.75	0.0272	16.30	0.0561
11.02	0.0312	18.65	0.0702
13.10	0.0378	20.80	0.0800
14.85	0.0438	23.30	0.0982
15.00	0.0456	24.70	0.1105
16.95	0.0575	Desorption	
16.95	0.0596	16.30	0.0655
Desorption		11.02	0.0319
11.02	0.0316		
6.95	0.0204		
2.90	0.0102		

RESULTS

The results of this investigation are given in tables 1 and 2. In each table the column headed x/m gives the grams of adsorbed material per

TABLE 2

Adsorption of iodine

Pressure of iodine = 17 mm.; weight of gel sample = 0.5700 g.

T	x/m
degrees C.	
85	0.0930
92.5	0.0591
100	0.0368
115	0.0198
130	0.0114
137.5	0.0088

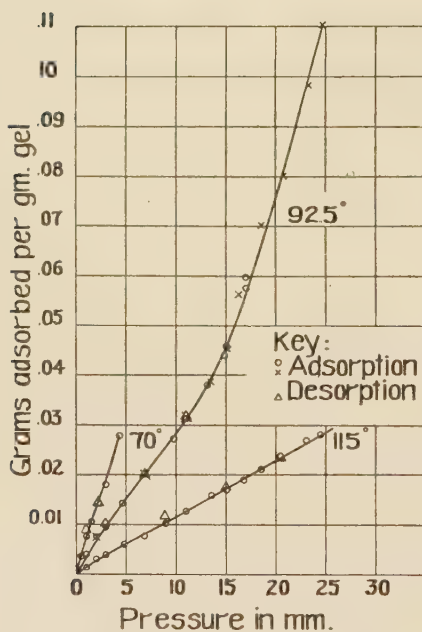


FIG. 2. IODINE ISOTHERMS

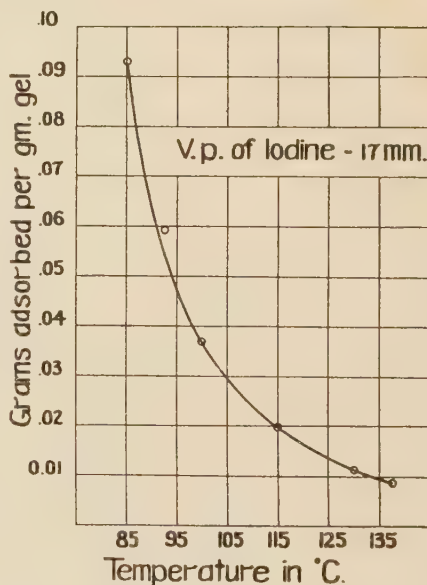


FIG. 3. IODINE ISOBAR

gram of gel and the column headed p gives the equilibrium pressure in millimeters of mercury.

Table 1 gives the results for the three iodine isotherms at 70°, 92.5°, and 115°C., using the same sample of gel. In this way comparable results can

be obtained. Figure 2 shows graphically the results of the first table. It is to be noted that a decided break in the curve of the 92.5°C. isotherm occurs at a pressure of about 11 mm. The curve of the 70°C. isotherm also bends noticeably upwards.

In table 2 are given the results of keeping the pressure of the iodine constant (17 mm.) and varying the temperature of the gel. These results are shown graphically in figure 3. This isobar is a smooth curve showing the normal behavior, i.e., a decrease in adsorption with an increase in temperature. The value of the water content of the gel was found to be 2.3 per cent.

DISCUSSION

The experimental work was performed in such a manner as to lead us to believe that we were in all cases dealing with true equilibrium phenomena. This criterion of real equilibrium is important, as so much erroneous adsorption theory has been drawn from faulty experimental data.

Our experiments show that the adsorption of iodine vapor decreases as we increase the temperature. This is normal behavior and is not in accord with the postulate that we proposed at the outset of this work. We expected to find an increase in the adsorption of iodine vapor above the normal melting point of iodine. However, we did observe a decided increase in adsorption in the case of the 92.5°C. isotherm when the pressure of the iodine exceeded 11 mm. We shall limit our discussion to this isotherm, inasmuch as experimental conditions made it possible for us to work over a sufficient range of pressures only at this temperature. Our explanation of the increase of adsorption at 11 mm. pressure on the 92.5°C. adsorption isotherm is that, at this pressure and temperature, liquid iodine is present in the capillaries of the silica gel, notwithstanding the fact that the ordinary melting point of iodine is 21.5°C. higher. It is to be noted that our quantitative calculations must necessarily be clothed with considerable uncertainties, owing to our lack of knowledge of the physical constants of matter in the state of highly curved surfaces. In other words, it is not safe to assume that the density, surface tension, or latent heat of vaporization of liquids in very small capillaries are the same as the normal values.

Let us consider the case of solid iodine in contact through the vapor phase with liquid iodine wetting a small capillary. The problem is to find the temperature at which the two phases of iodine have the same vapor pressure. It is known that the surface energy of the liquid iodine will operate in such a manner as to reduce the vapor pressure of the liquid. Consequently, the temperature of the solid iodine must be reduced below the normal melting point (114°C.) in order to maintain equilibrium. If we assume that the solid iodine is not affected by capillary forces while the liquid iodine is, the thermodynamic treatment is as follows:

The change in free energy of the solid and liquid (denoting the states respectively by the subscripts s and l) is,

$$\begin{aligned} dF_s &= \left(\frac{\partial F}{\partial T} \right)_p dT = -S_s dT \\ dF_l &= \left(\frac{\partial F}{\partial T} \right)_p dT + \left(\frac{\partial F}{\partial p} \right)_T dp \\ &= -S_l dT + V_l dp \end{aligned}$$

At the melting point $dF_s = dF_l$. Here dp is the change in the hydrostatic pressure on the liquid and we shall denote it by $d\pi$,

$$V_l d\pi = (S_l - S_s) dT$$

$$V_l d\pi = \frac{L_F}{T} dT$$

Integrating this expression between the limits π_1 and π_2 and T_1 and T_2 ,

$$V_l (\pi_2 - \pi_1) = L_F \ln \frac{T_2}{T_1}$$

In other words, we are able to calculate the temperature to which the system must be lowered in order to maintain equilibrium when the liquid iodine is under a known pressure.

We are also able to calculate the pressure under which the liquid iodine finds itself, owing to the action of the capillary forces, by making use of the well-known thermodynamic equation of Gibbs,

$$\frac{dp}{d\pi} = \frac{v}{V}$$

which expresses the variation of the vapor pressure p , with the hydrostatic pressure π , in terms of the specific volumes of the liquid v , and the vapor V . In our case the anomalous behavior begins at a pressure of 11 mm. and at a temperature of 92.5°C. Inasmuch as the following calculations are only approximate and as we wish to make sure that we are actually dealing with liquid iodine in the pores rather than with a monomolecular adsorbed layer which represents the phenomenon during the first stages of the adsorption, we have selected 20 mm. as the equilibrium pressure in our calculation. Before we can calculate the lowering of the vapor pressure of liquid iodine produced by capillarity, we must first know the vapor pressure of liquid or supercooled iodine at this temperature. This can be found by an extrapolation of the vapor pressure curve of liquid iodine or by means of the Clausius-Clapeyron equation. By neglecting the molal volume of

the liquid by comparison with the molal volume of vapor and by assuming the vapor to be an ideal gas, the integrated form of this equation is,

$$2.3 \log \frac{p_2}{p_1} = \frac{L_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Assuming the normal value for the latent heat of vaporization, 10,500 cal. per mole (International Critical Tables), and substituting the following values in the above equation,

$$p_1 = 90.1 \text{ mm.} \quad T_1 = 114^\circ + 273^\circ = 387^\circ\text{K.}$$

$$T_2 = 92.5^\circ + 273^\circ = 365.5^\circ\text{K.}$$

it is calculated that liquid iodine at 92.5°C. would have a vapor pressure of 39.8 mm. Extrapolation of the vapor pressure curve of liquid iodine gives the same value. Therefore the lowering of the vapor pressure amounts to (39.8 - 20) or 19.8 mm. Substituting the values,

$$p_2 - p_1 = -19.8 \text{ mm.} \quad v = \frac{254}{4.0} = 63.5 \text{ cc. per mole}$$

$$\pi_1 = 0$$

$$V = \frac{RT}{p} = 11.4 \times 10^5 \text{ cc. per mole}$$

in the integrated form of the Gibbs equation,

$$p_2 - p_1 = \frac{v}{V} (\pi_2 - \pi_1)$$

gives a negative hydrostatic pressure, π , of 470 atmospheres. To obtain this value, we assumed the density of the liquid iodine in the small capillary to be the same as that of liquid in bulk.

If this approximate value of the negative capillary pressure (470 atmospheres) is now substituted in the equation connecting melting temperature with pressure as previously developed, and where

$$\begin{array}{ll} \pi_1 = 0 & V = 63.5 \text{ cc. per mole} \\ \pi_2 = -470 \text{ atmospheres} & L_f = 4000 \text{ cal. per mole (I. C. T.)} \\ & T_1 = 114 + 273 = 387^\circ\text{K.} \end{array}$$

a melting temperature $T_2 = 323^\circ\text{K.}$ or 50°C. is obtained. A lowering of the melting point of iodine of 64°C. ($114^\circ\text{C.} - 50^\circ\text{C.}$) is indicated.

These calculations lead us to the conclusion that we are completely justified in our contention that it is possible for liquid iodine to exist in a capillary tube in which the vapor pressure of the liquid is only 20 mm. We have seen that our calculations would lead us to the conclusion of a lowering of the melting point of 64°C. This calculated value of the melting point lowering cannot be considered as accurate, owing to our lack of

knowledge of the proper value of the physical constants of liquid iodine in capillaries. We have assumed, for example, the normal density of liquid iodine in the capillaries; this is certain to be incorrect, inasmuch as the very nature of the change in vapor pressure produced by pressure is predicated upon a change in density of the condensed phase.

We have shown that it is possible for the liquid state to have a stable existence far below the normal melting point, provided sufficiently powerful capillary forces are in operation. It is evident that these forces must diminish in magnitude as the adsorption increases, i.e., as the pores fill it is necessary to assume increasing radii of curvature. Therefore, it is necessary to assume the existence of unstable liquid at some point higher on the adsorption isotherm.

SUMMARY

1. Measurements have been made of the adsorption of iodine vapor by silica gel at three temperatures.
2. The adsorption isotherm of iodine at 92.5°C. showed a pronounced flex upwards when a definite pressure was reached.
3. The above behavior was explained by the assumption of liquid iodine being present in the silica gel and wetting the walls of the same.
4. The effect of free surface energy on the solid-liquid transition temperature was thermodynamically explained.

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BIOGRAPHY

The author of this dissertation, W. Everett Land, was born in Baltimore, Maryland on August 23, 1908. He received his early education in the elementary schools of this city and the Baltimore Polytechnic Institute. In October, 1925, he entered the Johns Hopkins University and received the degree of Bachelor of Science in Chemistry in June, 1928. In 1929, he was admitted to the School of Higher Studies of the Faculty of Philosophy as a graduate student in chemistry.

